

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the production of Monohydroxy Polyethers of Polyhydric Alcohols

SPECIFICATION NO. 821,977

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are Wilhelm Krey, of Bahnhofstrasse 52, Krefeld-Uerdingen, Germany and Karl Raichle, of Stollwerckstrasse 22, Krefeld-Uerdingen, Germany, both of German nationality.

THE PATENT OFFICE,
30th October, 1959

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of an organic monohalide, the halogen of which is reactive and aliphatically bound, and a corresponding amount of an alkali metal hydroxide in the presence of water or benzene under pressure. In the presence of water, however, not

alcohols with at least 3 methyloxy, alkoxy, or arylmethyloxy groups on one carbon atom, such as the condensation products of formaldehyde

20		
40	with acetaldehyde	= pentaerythritol
	with propionaldehyde	= trimethylolethane
	with butyraldehyde	= trimethylolpropane
	with valeraldehyde	= trimethylolbutane
	with phenylacetaldehyde	= trimethylolphenylmethane
45	with acetone	= 3,3,3-trimethylolpropan-2-ol
	with methylethylketone	= 3,3-dimethylolbutan-2-ol
	with acetophenone	= 2,2,2-trimethylol-1-phenyl-ethanol
	with phenylethylketone	= 2,2-dimethylol-1-phenylpropanol

Furthermore, mono- and diethers of such polyhydric alcohols may be used provided that at least two hydroxyl groups of those ether-alcohols are still free. Examples of such ether-alcohols are: mono- and diethers of pentaerythritol, of 3,3,3-trimethylolpropan-2-ol and of 2,2,2-trimethylol-1-phenylethanol, and monoethers of trimethylol-ethane, -propane, and -butane, of trimethylolphenylmethane, of 3,3-dimethylolbutan-2-ol and of 2,2-dimethylol-1-phenylpropanol.

The ether-alcohols mentioned are especially suitable for the production of mixed polyethers. Thus, for example, the allyl-benzyl ether of trimethylol-propane can be obtained

by the reaction of one mol trimethylol-propane monoallyl ether with at least one mol of benzyl chloride and the corresponding amount of an alkali metal hydroxide.

As organic monohalides suitable for the present process, there may be used all monohalides known for this type of reaction, the halide atom of which is aliphatically bound and reactive. The halides of practical importance are the chlorides, although bromides and iodides can also be employed. As examples of suitable halides there may be mentioned: ethyl, propyl, isopropyl, *n*-butyl, and isobutyl, chloride, bromide and iodide, pentyl and hexyl chlorides, bromides and iodides, allyl,

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Process for the production of Monohydroxy Polyethers of Polyhydric Alcohols

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 22c Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the production of monohydroxy polyethers.

It is known to produce diethers of glycerol and triethers of pentaerythritol by reacting 1 mol of the polyalcohol having 2, 3 or 4 free hydroxyl groups with 1, 2 or 3 mol respectively of an organic monohalide, the halogen of which is reactive and aliphatically bound, and a corresponding amount of an alkali metal hydroxide in the presence of water or benzene under pressure. In the presence of water, however, not

40	with acetaldehyde	= pentaerythritol
	with propionaldehyde	= trimethylolethane
	with butyraldehyde	= trimethylolpropane
	with valeraldehyde	= trimethylolbutane
	with phenylacetaldehyde	= trimethylolphenylmethane
45	with acetone	= 3,3,3-trimethylolpropan-2-ol
	with methylethylketone	= 3,3-dimethylolbutan-2-ol
	with acetophenone	= 2,2,2-trimethylol-1-phenyl-ethanol
	with phenylethylketone	= 2,2-dimethylol-1-phenylpropanol

Furthermore, mono- and diethers of such polyhydric alcohols may be used provided that at least two hydroxyl groups of those ether-alcohols are still free. Examples of such ether-alcohols are: mono- and diethers of pentaerythritol, of 3,3,3-trimethylolpropan-2-ol and of 2,2,2-trimethylol-1-phenylethanol, and monoethers of trimethylol-ethane, -propane, and -butane, of trimethylolphenylmethane, of 3,3-dimethylolbutan-2-ol and of 2,2-dimethylol-1-phenylpropanol.

The ether-alcohols mentioned are especially suitable for the production of mixed polyethers. Thus, for example, the allyl-benzyl ether of trimethylolpropane can be obtained

only the formation of the ether takes place but a hydrolysis of the halide also occurs to a substantial degree. On the other hand, however, the use of benzene or of a similar volatile solvent makes the use of an autoclave necessary.

We have now found that the above-mentioned ether formation can be improved by working in the absence of water or of a volatile solvent and preferably carrying out the reaction in the presence of a polyether of the kind described.

The process according to the present invention is applicable to all polyalcohols which are obtainable by the condensation of aldehydes or ketones with formaldehyde, i.e. all polyalcohols with at least 3 methylol, alkylmethylol or arylmethylol groups on one carbon atom, such as the condensation products of formaldehyde

by the reaction of one mol trimethylolpropane monoallyl ether with at least one mol of benzyl chloride and the corresponding amount of an alkali metal hydroxide.

As organic monohalides suitable for the present process, there may be used all monohalides known for this type of reaction, the halide atom of which is aliphatically bound and reactive. The halides of practical importance are the chlorides, although bromides and iodides can also be employed. As examples of suitable halides there may be mentioned: ethyl, propyl, isopropyl, n-butyl, and isobutyl, chloride, bromide and iodide, pentyl and hexyl chlorides, bromides and iodides, allyl,

5 α - and β -methallyl, crotyl, pentenyl and hexenyl chloride, bromides and iodides, cyclopentyl, cyclohexyl, cyclopentenyl and cyclohexenyl chlorides, bromides, and iodides, benzyl chloride and bromide, α - and β -phenyl ethyl and di-phenyl methyl chloride and bromide, and chloro- and bromoethyl naphthalenes.

10 Suitable reaction temperatures range from room temperature to about 200° C., and preferably from about 50 to about 150° C.

As already mentioned, in some cases it is advantageous to add to the reaction mixture a polyether of the mentioned type as a diluent. For this purpose, it is expedient to choose a polyether the boiling point of which is sufficiently above or below that of the polyether to be produced to enable the latter to be separated by fractionation. Thus, for example, the dibenzyl ether of trimethylolpropane is a suitable diluent in the production of the corresponding dibutyl ether. However, it is also advantageous to use as a diluent the polyether to be produced. Thus, for example, the diallyl ether of trimethylolpropane for the production of this ether alcohol.

The monohydroxy-diethers obtainable by the process according to the present invention are valuable solvents for a great number of organic compounds and can, therefore, be used in the production of lacquers. They may further be used as intermediates for the production of, for example, modified polyesters by methods well known *per se*.

35 The following examples are given for the purpose of illustrating the invention.

EXAMPLE 1

40 In a vessel provided with stirrer, heating and cooling arrangement, 1340 parts by weight (10 mols) of trimethylolpropane are heated to 60–70° C. For production of the diallyl ether there are required when using a 10 per cent excess of the reagents: 1670 parts by weight of allyl chloride and 880 parts by weight of sodium hydroxide. Since the reaction mixture would solidify by the addition of the whole amount of sodium hydroxide, only 220 parts by weight of sodium hydroxide are initially added to the alcohol and the mixture is stirred at 60–70° C. for about 1 hour until the alcoholate is formed. Subsequently, 417.5 parts by weight of allyl chloride are likewise introduced at 60–70° C. as at the rate of which it is consumed. The process may be carried out in an open vessel under reflux or the allyl chloride may be forced into a closed vessel, involving an excess pressure of about 0.1 to 1 atmosphere. The procedure is repeated three times until the total quantity of sodium hydroxide and of allyl chloride has reacted. Stirring is continued at 60–70° C. for a further 1–2 hours, the mixture is neutralised with a little

acid (mineral acid or acetic acid), washed 65 with 2500 parts by weight of water in order to remove the salts, and the impure product thus obtained is fractionated. By distillation under normal pressure, 150 parts by weight of allyl chloride are recovered. The remaining part is distilled *in vacuo* yielding 2000 parts by weight of the diallyl ether of trimethylolpropane (b.p. about 95 to 105° C./2–5 mm Hg). The hydroxyl value lies at 260–270 (theoretical value 262).

75 It is more convenient to carry out the reaction by adding as solvent 600 parts by weight of trimethylolpropane diallyl ether to the composition. The whole quantity of sodium hydroxide may then be added in one portion; the allyl chloride is likewise introduced in one portion at the speed at which it is consumed. The working up is not changed and the yield remains the same.

EXAMPLE 2

85 The process is carried out as described in Example 1 but the allyl chloride is replaced by 2785 parts by weight of benzyl chloride (=2 mols + 10 per cent excess). By fractionating the impure product 230 grams of benzyl chloride are recovered and 4450 parts by weight of trimethylolpropane-dibenzyl ether (b.p. 195–205° C./1–2 mm Hg) are obtained, hydroxyl value 180 to 185 (theoretically 178).

EXAMPLE 3

95 If the 1670 parts by weight of allyl chloride are replaced in Example 1 by 2640 parts by weight of allyl bromide, the same yield of diallyl ether is obtained by the same working method.

EXAMPLE 4

105 In a 3 litre-pressure vessel made of chromium-nickel steel and provided with a good stirrer, there are heated to 150° C. for 4 hours, 402 grams of trimethylolpropane (3 mols), 400 grams of trimethylolpropane-dibenzyl ether as diluting agent, 290 grams of sodium hydroxide (6 mols + 20 per cent excess) and 665 grams of *n*-butyl chloride (6 mols + 20 per cent excess). Upon cooling, the mixture is neutralised with a small quantity of hydrochloric acid and the sodium chloride which separates out is filtered off. By fractionating the solution *in vacuo*, about 400 grams of trimethylolpropane-dibutyl ether, b.p. 120–140° C./1–2 mm Hg., are obtained. The dibenzyl ether remains in the residue and may be recovered in a pure state by distillation.

EXAMPLE 5

125 360 parts by weight of trimethylol ethane, boiling point 190° C., (3 mols) are reacted with vigorous stirring at 70–100° C. under reflux in the presence of 300 parts by weight of trimethylolethane-diallyl ether, with 300 parts by weight of sodium hydroxide (6 mols + 20 per cent excess) and 576 parts by

weight of allyl chloride (6 mols + 20 per cent excess). The mixture is treated with water in order to dissolve the precipitated sodium chloride and the aqueous solution is then separated. By fractional distillation, there are obtained (after removing the diallyl ether used as solvent) 560 grams of trimethylol-ethane-diallyl ether of b.p. 95—105° C./2—5 mm Hg. Hydroxyl value 290—295 (theoretically 280).

EXAMPLE 6

If 405 parts by weight of trimethylolpropane (3 mols) are reacted in a similar manner to that described in Example 5, with 275 parts by weight of sodium hydroxide (6 mols + 10 per cent excess) and 600 parts by weight of α -methallyl chloride (6 mols + 10 per cent excess) in the presence of 200 parts by weight of trimethylolpropane-dibenzyl ether, there is obtained after washing out the sodium chloride with water an oil which yields upon fractionating about 520 parts by weight of trimethylolpropane-di- α -methallyl ether of b.p. 102—105° C./0.2 mm Hg. The dibenzyl ether remaining in the residue is recovered unchanged by distillation.

EXAMPLE 7

698 parts by weight of trimethylolpropane-monoallyl ether (4 mols) are stirred at 80—100° C. with 200 parts by weight of 97 per cent sodium hydroxide (4.2 mols). At the same temperature, 600 parts by weight of benzyl chloride (4.2 mols) are added dropwise. When the strongly exothermic reaction has subsided, the precipitated sodium chloride is dissolved by the addition of 1000 parts by weight of water and the aqueous layer is separated. By distilling the raw product, 860 parts by weight (82 per cent of the theoretical) of the mixed ether having a hydroxyl value 220 to 240 (theoretical value 221) are obtained.

EXAMPLE 8

To a mixture of 272 grams of pentaerythritol (2 mols) and 347 grams of sodium hydroxide there are added at 80—100° C. 641 grams of allyl chloride (6 mols + 182 grams excess) at the rate at which the allyl chloride reacts. The process takes 6—8 hours. Then xylene is added to the reaction mixture, the sodium chloride is filtered off and the filtrate fractionated under reduced pressure. Firstly the excess of allyl chloride and the xylene distil off. 470 grams of the raw poly-ether then are fractionated as follows:—

329 grams = 70 per cent of monohydroxy triallyl ether (b.p. 126—130° C./1—2 mm Hg).
118 grams = 25 per cent of dihydroxy diallyl ether (b.p. 139—144° C./1—2 mm Hg).
5 grams = 1 per cent of trihydroxy monoallyl ether (b.p. 163—170° C./1—2 mm Hg).
15 grams = 3 per cent of residue.

Variations are possible when carrying out the reaction. Thus, when using about 100—400 grams of pentaerythritol triallyl ether (pure or in mixture with di- and monoether) as dilution agent, the reaction time is reduced to about the half.

Furthermore, the mono- and di-ethers of pentaerythritol can be reacted in a corresponding manner and, in this way, mixed triethers are produced.

EXAMPLE 9

To a solution of 226 grams (1 mol) of pentaerythritol monobenzyl ether (b.p. 190° C./0.4 mm Hg) in 300 grams of trimethylolpropane diallyl ether 96 grams of caustic soda (2 mols + 16 grams excess) and 183 grams of allyl chloride (2 mols + 31 grams excess) are added at 60—80° C. with stirring. When all the allyl chloride is added, i.e. after about 1—2 hours, the stirring is continued for a further hour at 60—80° C. Then the mixture is neutralised by hydrochloric acid and washed with water. The organic layer is separated and fractionated. One obtains at atmospheric pressure 20 grams of unreacted allyl chloride and, under reduced pressure, firstly the trimethylolpropane diallyl ether. At 180—185° C./3 mm Hg 270—280 grams of pentaerythritol monobenzyl diallyl ether distill off. The hydroxyl number of the product is 188—189 (theoretical value 186).

EXAMPLE 10

To 430 grams (2 mols) of pentaerythritol diallyl ether there are added 96 grams of pulverised caustic soda (2 mols + 16 grams excess). The mixture is heated at 60—90° C. with stirring and 302 grams of benzyl chloride (2 mols + 50 grams excess) are added dropwise during 3—4 hours. The stirring is continued for another hour at the same temperature. The residue of sodium chloride is then filtered off, the filtrate washed with water and fractionated. From 630 grams of the raw product 560 grams of pentaerythritol monobenzyl diallyl ether, identical with the product of Example 9, are obtained. Residue 50 grams.

EXAMPLE 11

To a solution of 134 grams (1 mol) of 3,3-dimethylolbutan-2-ol in 60 grams of pentaerythritol triallyl ether, 132 grams (3.3 mols) of caustic soda are added with stirring. Heated to 100° C., 252 grams (3.3 mols) of allyl chloride are added dropwise under reflux at such a rate that the reaction temperature does not drop below 80° C. When all the allyl chloride is added, the stirring is continued for 7 hours at 80° C. The mixture is then neutralised with hydrochloric acid, and after the addition of 500 ccm. of toluene, the water is distilled off azeotropically. After filtering off the residue of sodium chloride the excess allyl chloride and toluene are recovered by distillation. By fractionating the residue under

reduced pressure 191 grams of the 3,3-diallyl ether of 3,3-dimethylol-butan-2-ol with a b.p. of 103° C. at 3 mm Hg are obtained, this being 89 per cent of the theoretical yield. 59 grams of the pentaerythritol triallyl ether used as diluting agent are recovered at 136° C. and 3 mm Hg.

WHAT WE CLAIM IS:—

1. Process for the production of monohydroxypolyethers derived from polyhydric alcohols having at least 3 methylol, alkylmethylol or arylmethylol groups on 1 carbon atom by reacting 1 mol of such a polyhydric alcohol having 2, 3 or 4 free hydroxyl groups and 2, 1 or 0 etherified hydroxyl groups with at least 1, 2 or 3 mols, respectively, of an organic monohalide, the halide atom of which is aliphatically bound and reactive, and of an alkali metal hydroxide at a temperature of from 15° C. to 200° C., characterised in that the reaction is carried out in the absence of water and of a volatile solvent.
2. Process according to Claim 1, wherein a polyether of the type described is used as a diluent for the reaction mixture.
3. Process according to Claim 2, wherein a polyether added to the reaction mixture as diluent has a boiling point lower or higher enough than the polyether to be produced, thus enabling the separation of the two polyethers present in the mixture at the end of the reaction by fractional distillation.
4. Process according to Claim 2, wherein the polyether added to the reaction mixture as diluent is the polyether to be produced.
5. Process for the production of polyethers, substantially as hereinbefore described with reference to any of the specific examples.
6. Diethers derived from trihydric alcohols having 3 methylol alkylmethylol or arylmethylol groups attached to the same carbon atom.
7. Mixed diethers derived from trihydric alcohols having 3 methylol, alkylmethylol or arylmethylol groups on 1 carbon atom.
8. Diethers substantially as hereinbefore described with reference to any one of the foregoing examples.
9. Monohydroxy polyethers, whenever produced by the process according to any of Claims 1—5.

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